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TO Mr. S. H. Smiley

LOCATION

DATE March 2, 1955

ANSWERING LETTER DATE

ATTENTION

SUBJECT Recovery of Fluorine From Feed Plant Vent Gases

G 780

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INTRODUCTION

At the present time, at least 10% of the fluorine generated for use in the manufacture of uranium hexafluoride is unavoidably lost in the vent gases from the process. The recovery of this fluorine has become of prime importance since the expansion of the uranium hexafluoride manufacturing facilities to the 48 tons of uranium per day production level. The estimated cost of the vented fluorine will amount to $400,000 per year based on the above percentage lost and a cost per pound of $0.65.

Data collected at K-25 on tower reactors designed for fluorine recovery have indicated that essentially complete removal of fluorine from a gas stream is possible if the fluorine and uranium tetrafluoride feed rates are accurately balanced, or if an excess of powder is employed. However, operational tests in K-1131, using a countercurrent flow of reactants in a 4-inch diameter reactor, showed that a fluorine recovery system must

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be able to tolerate both wide variations in fluorine flow and a moderate dust burden in the outlet gas stream. An experimental recovery unit designed to meet the above criteria has been built and is undergoing test in the K-1413 Engineering Development Laboratory.

PROCESS EQUIPMENT AND FLOW

In essence, the unit consists of (1) a concurrent fluorination tower, operated with a large powder excess to assure complete utilization of all the fluorine regardless of variations in flow*; (2) a ribbon-flight screw conveyor, designed to cool the reactants to the point at which no further interaction takes place while maintaining the solids as a finely divided powder; and (3) a barrier filter, located after the screw to remove the dust from the gas stream. Figure 1 is a schematic flow diagram of the pilot plant system.

In operation, a fluorine-air mixture is reacted in the tower with an excess of uranium tetrafluoride powder to form uranium hexafluoride gas and some intermediate uranium fluorides. The reaction products are then cooled in the screw conveyor, which is mounted directly below the tower, and a partial separation of the uranium hexafluoride and ash is attained. The gas stream leaves the screw at a temperature of 400^{o}F. or less and passes through the porous-tube filter, where the final separation of gas and solids takes place, to the cold traps which collect the uranium hexafluoride. The remaining gases, consisting primarily of oxygen, nitrogen, and hydrogen fluoride, are vented to the atmosphere.

The solids in the screw are discharged through a plug valve into an ash receiver. The material deposited on the filter tubes is dislodged by periodic back-blowing with high pressure air and falls into the same ash receiver.

RESULTS

As of January 26, 1955, thirteen tests were completed, with the longest period of operation being 28-1/2 hours, and with uranium tetrafluoride excesses as high as 115%. The results of the pilot plant runs are presented in table I. The fluorine recovery, in all runs except TSR-1, was essentially complete in that the concentration of fluorine in the outlet gas was less than 0.05 mol per cent, the minimum amount detectable by the analytical method employed. The ash from the runs varied somewhat in composition (table II), but was mainly a mixture of uranium tetrafluoride and the intermediate, uranium pentafluoride. Sieve analyses of the ash showed some large particles (table III) but not enough to cause operational difficulty when the ash is blended with fresh uranium tetrafluoride and burned in the primary reactors. A short summary of each experimental test follows.

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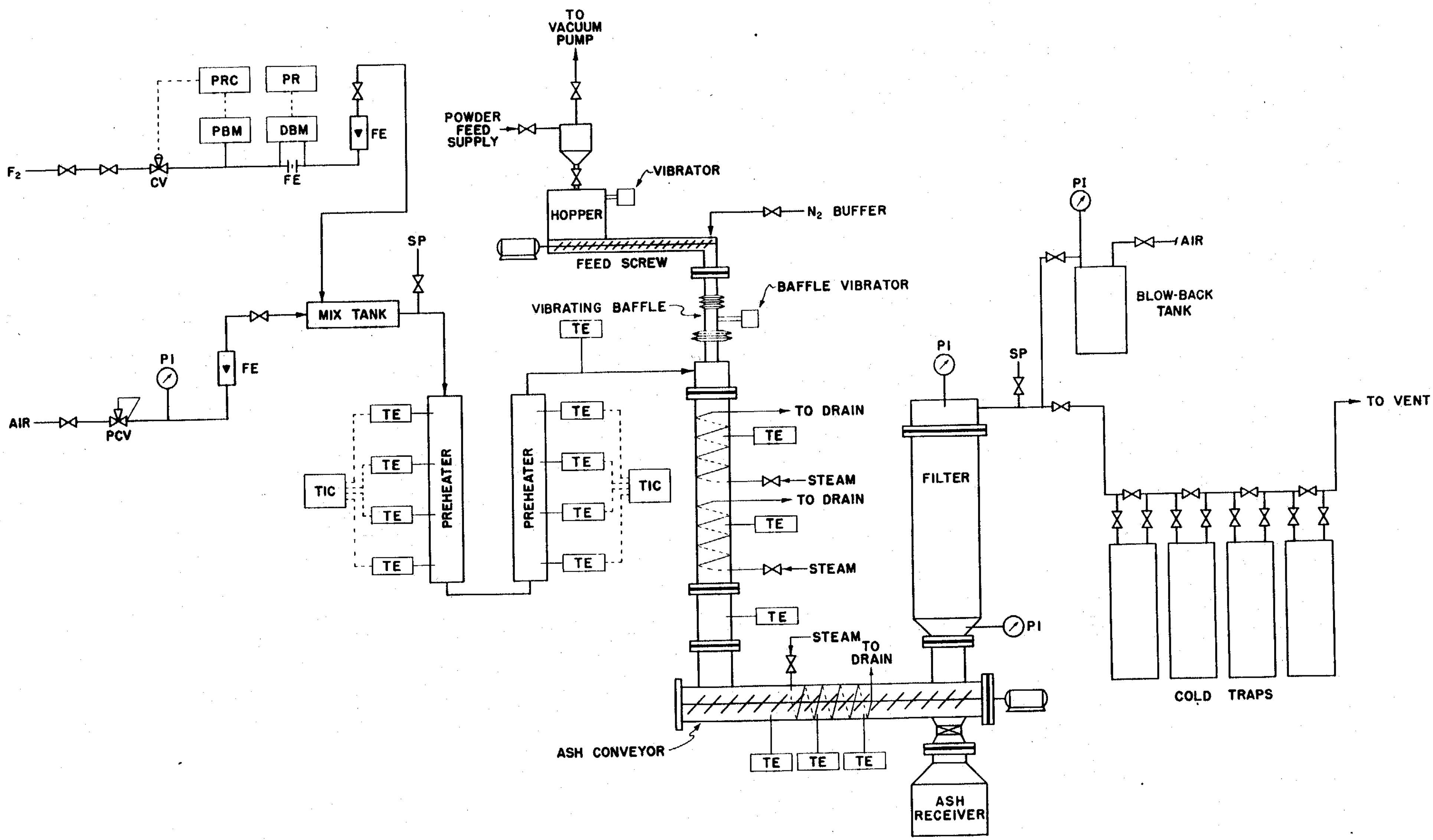
* In the production plant, the excess uranium tetrafluoride from the recovery unit will be mixed with the fresh uranium tetrafluoride feed and burned to uranium hexafluoride in the primary tower reactors.



FLOW & INSTRUMENTATION DIAGRAM
FOR FLUORINE CLEAN-UP UNIT USING ASH RECYCLE

TABLE I

Fluorine Recovery Unit - Run Summary

Run No.	Length Of Run Hours	UF_4 Rate lbs./hr.	F_2 Rate lbs./hr.	Powder Excess, %	Slag Removed, lbs.	F_2 To Ash %	F_2 Inlet Conc. %	F_2 Outlet Conc. %	Comments
TSR-1	1.25	116	13.6	7.5		19.4	33.3	3.8	Shakedown run - poor baffle vibration.
TSR-2	1.83	105	11.8	12.0		11.1	31.9	<0.05	Ran O.K.
TSR-3	3.50	117	14.1	25.0		26.8	31.8	<0.05	Ran O.K. Screw failed mechanically.
TSR-4	5.25	117	15.2	15.0	Not Weighed	14.0	33.7	<0.05	Interrupted at 3.1 hours. Vibrator failed. Shutdown O.K.
TSR-5	14.25	117	15.7	10.0	34	8.0	32.0	<0.05	Ash screw failed. Shaftless section.
TSR-6	8.33	115	11.5	76.5	91	39.2	33.4	<0.05	Ash discharge valve and tower plugged.
TSR-7	15.10	110	13.25	50.0	74.5	24.0	28.2	<0.05	Barrier filter plugged at 7.1 hours. Fluorine supply low.
TSR-8	4.90		14.2	43.5			29.5	<0.05	Low Fluorine supply made it necessary to cut flow rate at 4.9 hours.
TSR-8a	3.90	109	9.5	115.0	90	44.5	28.1	<0.05	Tower plugged at shutdown.
TSR-9	6.20	119	20.1	17.0		12.7	25.8	<0.05	Shut down to check ash screw. O.K.
TSR-10	4.20	127	15.1	56.0	55	32.0	24.6	<0.05	Restart of run TSR-9 with higher powder rate.
TSR-11	9.00	113	13.4	52.0	74.25	24.8	24.6	<0.05	Interrupted by cold trap plug. Start-ups were with 4% excess.
TSR-12	14.25		11.7	26.0			26.1	<0.05	Three starts due to vibrator failure. Cut fluorine flow due to improved uranium tetrafluoride assay at 14-1/4 hours. 23 hours continuous operation attained.
TSR-12a	14.25	84.5	9.75	35.0	97.25		28.1	<0.05	
TSR-13	11.0	83.5	9.3	44.0	30	19.8	26.8	<0.05	First run with short tower. Plugged above fluorine inlet.

Runs TSR-1 and 2 were made with uranium tetrafluoride manufactured from hydrate activated oxide; TSR-3, 4, and 5 made with uranium tetrafluoride manufactured from Hanford oxide; and the remaining runs made with uranium tetrafluoride from Savannah River oxide.

TABLE II

Typical Chemical Analyses On
Ash From Fluorine Recovery Runs

Run Number	TSR-5	TSR-6	TSR-7	TSR-8	TSR-8a	TSR-12	TSR-12a	TSR-13
Per Cent U	69.4	74.2	74.0	73.3	74.2	73.0	73.0	73.5
Per Cent U^{+4}	39.7	43.0	46.5	43.4	44.3	40.1	37.5	41.3
Per Cent F	26.5	24.5	25.1	26.2	25.3	27.0	26.0	24.5

TABLE III

Typical Sieve Analyses on
Ash From Fluorine Recovery Unit

		Run Number				
Mesh Size	Feed UF_4	TSR-3	TSR-4	TSR-5	TSR-6	TSR-7
+ 20	3.5	3.9	6.6	12.9	11.2	2.3
+ 40	0.9	5.6	15.8	12.9	7.0	2.3
+ 80	1.4	15.6	22.8	20.5	11.8	7.1
+ 100	0.6	8.7	4.2	3.4	4.4	3.1
- 100	93.6	66.2	50.6	50.2	65.6	85.1

The first two runs, TSR-1 and 2, were made with low density uranium tetrafluoride to check the tower operation. The 3.8% fluorine in the outlet gas in run TSR-1 was found to be the result of poor powder dispersion, which was corrected in run TSR-2 by increasing the amplitude of vibration on the baffle assembly. In the next three runs, TSR-3, 4, and 5, made with uranium tetrafluoride processed from Hanford uranium trioxide in the vibrating trays at the Paducah feed plant, complete fluorine utilization was realized. The average fluorine concentration in the inlet gas was 33% and the powder excesses were 25, 15, and 10%, respectively (uranium tetrafluoride feed rate of 117 pounds per hour).

Inspection of the tower at the completion of run TSR-4 showed two large lumps of caked material about 1-1/2 inches deep, at the top and the middle of the tower. The remainder of the surface had a smooth deposit increasing from 1/8 inch deep at the top of the tower to 1/2 inch deep at the bottom.

The composition of the deposit appeared to vary along the length of the tower, with the material at the top being light green in color and easily dislodged, and the material at the bottom being black, crystalline, and extremely hard to remove.

In run TSR-5, the tower plugged completely after 14-1/4 hours of satisfactory operation. Inspection of the ash screw revealed that the portion of the screw flight* directly under the tower outlet had twisted free from the shaft, with the result that ash accumulated at this point and plugged the lower end of the tower. The remainder of the tower was fouled in a similar to that described above for run TSR-4. A total of 34 pounds of slag was removed from the tower proper.

The damaged screw was replaced with a flight having a larger diameter shaft that extended the full length of the screw, instead of stopping at the tower outlet as in the previous design. This was done to determine whether the slag would build up on the shaft, as had been theorized. Run TSR-6, made with the redesigned screw, was terminated after 8-1/3 hours operation by a tower plug. Inspection of the tower and screw showed that the ash discharge valve had plugged, and the powder accumulation at the outlet of the screw had stopped the gas flow. In addition, a severe slag build-up was found on the section of the shaft located under the tower outlet. The screw was therefore altered to conform to the original design, except that the shaftless section was strengthened by welding longitudinal scrapers to the ribbon.

The next run, TSR-7, was interrupted after 7.1 hours of operation by a plug in the barrier filter. The filter was disassembled and the open spaces between the barrier tubes were found to be packed tightly with a fine powder which was easily removed by shaking the bundle. Several of the tubes were

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* A shaftless screw flight was used directly under the tower outlet, since it was felt that a shaft in this location would slag badly due to the impingement of semi-molten solids from the tower outlet. This was later shown to be true in run TSR-6.

damaged in removing the bundle, however, and it was necessary to replace the unit. The run was then resumed and the system operated satisfactorily until the fluorine supply was exhausted. At the end of the run (15.1 hours of operation), the screw was inspected and was found to be free of slag. The tower, however, was severely fouled with some of the deposits being 2 inches thick. A total of 74-1/2 pounds of material was removed from the walls.

To prevent further trouble with plugging of the filter, a blow-back system, consisting of a small surge tank connected to a source of 100 pounds air pressure and to the discharge side of the barrier filter, was installed so that the accumulation of powder on the barrier tubes could be dislodged while the tower was operating. The blow-back system was operated as follows:

1. The surge tank was filled to 100 psig., and the inlet valve was closed.

2. The recovery tower inlet and outlet valves were closed, and the powder feed was shut off.

3. The outlet valve from the surge tank was opened rapidly and was then closed after the pressures were equalized.

4. Steps 1 and 3 were repeated.

The off-stream time of the tower during the blow-back operation was less than 2 minutes, and the filter was blown back every 4 hours. Inspection of the filter at the completion of each run since the installation of this system has shown no significant build-up of ash on the tubes.

In run TSR-8, it was necessary to decrease the fluorine flow by about 33% after 4.9 hours of operation and thus increase the powder excess from 43.5 to 115% for the last 3.9 hours. The run was stopped by a leak in the air buffer line to the baffle assembly and, upon attempting to resume operation, it was found that the tower had plugged. The plug was located at the tower outlet, and had apparently formed when some of the material in the upper part of the tower broke loose and filled the tower outlet. Ninety pounds of slag were removed from the reactor.

It was noted that the lower part of the tower contained the greatest amount of slag. Since this section operated at a lower temperature than the remainder of the tower, it was believed that the amount of slagging would be decreased if the entire unit were kept hot (above 800°F.). The next few runs (TSR-9, 10, and 11) were therefore made with increased powder and fluorine rates in an attempt to raise the reactor wall temperature.

Run TSR-9 was shut down after 6.9 hours for inspection of the screw and ash discharge line. It was found that the powder feed rate had been low (only 17% excess instead of the desired 50%), and that the tower was relatively free of slag accumulation. Run TSR-10 was therefore started at an increased powder rate, without cleaning the tower. This run was shut down after 4.2 hours because the fluorine supply was low and a plug at the ash discharge point was indicated. A total of 55 pounds of slag was removed during clean-up. The next run (TSR-11) was made with a low uranium tetrafluoride excess (about 4%) during the start-up period in an attempt to minimize slagging by limiting the time the tower operated cold with a high powder excess. The total operating time for the run was 9 hours with one interruption caused by a cold trap plug and, except for the two start-ups, the uranium tetrafluoride excess was 52%. Operation was stopped by a plug in the ash discharge valve*. A total of 74-1/4 pounds of slag, consisting of a very hard material about 1 inch thick, was removed from the tower.

In the above runs, it was impossible to attain the desired wall temperatures by increasing the reactant flows and much of the lower part of the reactor was not above 650°F. For this reason, external heaters were added to the walls for the next series of tests and it was possible to hold all but a few points near the bottom of the tower to a minimum of 800°F. The unit was then operated successfully for 28-1/2 hours (run TSR-12). Inspection of the tower at the completion of the run showed a build-up of cake on the walls starting 18 inches from the top and ranging in thickness from 1/2 to 1-1/2 inches. The minimum open diameter of the tower was 2 inches. The accumulations of slag in the top 7 feet of the tower were soft, but the deposit below this was hard and difficult to remove. Eighty per cent of the 97-1/4 pounds removed was in the lower 3 feet of the tower.

The results of the run were calculated for two periods of 14-1/4 hours duration each, since it was necessary to reduce the fluorine flow at the midpoint of the run due to an improvement in the assay of the feed uranium tetrafluoride. The uranium tetrafluoride excess was 26% during the first half of the run and 35% during the second half.

Since the amount of heat supplied to the lower part of the column was not sufficient to hold all points above the desired minimum of 800°F. and, since previous experience with tower reactors has shown that 5 feet of tower is sufficient for the reaction of uranium tetrafluoride with an excess of fluorine, it was decided to shorten the effective length of the recovery tower to 7 feet by relocating the fluorine inlet. This system operated well for 11 hours (TSR-13) with a fluorine concentration of less than 0.05% in the outlet gas. A powder plug, which developed above the fluorine inlet, caused the shutdown. Inspection of the tower below this point revealed a comparatively uniform coating of soft cake on the walls and only 30 pounds of powder were removed from the reactor.

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* The ash discharge valve was replaced with a larger size valve at the completion of this run and no further trouble with plugs at this location has occurred.

SUMMARY

In summary, the investigation to date has shown (1) that slagging of the tower walls is a definite problem, particularly at the higher powder excesses, and that it may be necessary to shut down periodically and deslag the tower; (2) that slagging can be decreased by increasing the reactor wall temperature; (3) that complete reaction of all the fluorine is possible with powder excesses as low as 10%; (4) that a ribbon-flight screw is feasible for transporting and cooling reactor-ash and off-gases; (5) that a porous tube gas-filter can be operated successfully in a reactor of this nature, if a blow-back system is incorporated in the design; and (6) that the ash formed is relatively free from lumps and would require no further processing before being blended with the fresh uniform tetrafluoride feed to the primary towers.

Future plans for testing the unit include (1) operation at lower powder excesses using the full tower length of 10 feet; (2) the introduction of a blanket of air along the walls in the lower section of the tower to decrease the uranium hexafluoride concentration and to inhibit the formation of uranium fluoride intermediates; and (3) the installation of a short (about 7 feet long) tower with an expanded section at the bottom.

C. C. Littlefield
C. C. Littlefield
Engineering Development Department

/mbc